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October 9, 1963

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1934
Winter Session, Florida
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CITRUS
PROCESSING CONFERENCE

Held at
Florida Room, Citrus Building
Winter Haven, Florida

October 9, 1963

Agricultural Research Service

UNITED STATES DEPARTMENT OF AGRICULTURE

SOUTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION
Post Office Box 19687
New Orleans, Louisiana 70119

PROGRAM AND ABSTRACTS OF PAPERS

CITRUS PROCESSING CONFERENCE

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ORGANIZATIONS PARTICIPATING
IN
1963 CITRUS PROCESSING CONFERENCE

SOUTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION

C. H. Fisher, Director

Fruit and Vegetable Products Laboratory, Winter Haven, Florida
U. S. Fruit and Vegetable Products Laboratory, Weslaco, Texas
Naval Stores Laboratory, Olustee, Florida

WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION

M. J. Copley, Director

Fruit and Vegetable Chemistry Laboratory, Pasadena, California
Western Regional Research Laboratory, Albany, California

PROGRAM

CITRUS PROCESSING CONFERENCE
October 9, 1963

9:00 A.M. Registration

9:30 A.M. Introduction and Welcome

Presiding: M. K. Veldhuis, Chief, Fruit and Vegetable Products
Laboratory, Southern Utilization Research and
Development Division

INVESTIGATION OF THE REARRANGED PRODUCTS FROM LIMONENE OXIDE
FOUND IN ORANGE OIL

R. L. Settine, G. L. Parks and G. L. K. Hunter
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Florida

COUPLED GAS CHROMATOGRAPHY AND MASS SPECTROSCOPY AS AN ADVANCED
ANALYTICAL METHOD FOR CITRUS ESSENTIAL OIL ANALYSIS

G. L. K. Hunter and W. B. Brogden, Jr.
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Florida

THE SESQUITERPENES OF LEMON OIL

W. D. MacLeod
Western Utilization Research and Development Division
Fruit and Vegetable Chemistry Laboratory
Pasadena, California

TERPENE RESEARCH IN THE NAVAL STORES LABORATORY

G. S. Fisher
Southern Utilization Research and Development Division
Naval Stores Laboratory
Olustee, Florida

NEUTRAL CONSTITUENTS OF ORANGE PEEL JUICE EXTRACT

Lyle J. Swift
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Florida

12:00 Luncheon

1:30 P.M.

Presiding: L. W. Mazzeno, Jr., Acting Assistant Director,
Southern Utilization Research and Development
Division

FOAM-MAT DRYING OF CITRUS AT ALBANY

R. P. Graham
Engineering and Development Laboratory
Western Utilization Research and Development Division
Albany, California

DEBITTERING GRAPEFRUIT JUICE BY MEANS OF SPECIFIC ADSORPTION
ON RESINS

F. P. Griffiths, George Redman and B. J. Lime
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Weslaco, Texas

FOAM-MAT DRIED ORANGE JUICE - FURTHER STUDIES OF DRYING
CONDITIONS AND STORAGE STABILITY

James H. Tatum, Owen W. Bissett, Charles J. Wagner, Jr.,
and Robert E. Berry
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Florida

FOAM-MAT DRIED GRAPEFRUIT JUICE - STUDIES OF FOAM PREPARATION
AND TIME AND TEMPERATURE OF DRYING

Robert E. Berry, Owen W. Bissett, Charles J. Wagner, Jr.,
and James H. Tatum
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Florida

INVESTIGATION OF THE REARRANGED PRODUCTS FROM LIMONENE
OXIDE FOUND IN ORANGE OIL

by

R. L. Settime, G. L. Parks, and G. L. K. Hunter
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Florida

The elucidation of the composition of orange oil has been the goal of many investigators. Because of the use of orange oil by food industry to impart the characteristic orange flavor to many products, it appears essential that the constituents of the oil be unequivocally identified so that their contributions to flavor can be determined. Quantitative evaluation of constituents is also necessary to permit detection of changes which occur during maturation, storage, and processing. Much of the work in this region using gas chromatography, preparation of dinitrophenylhydrazine derivatives, and various other chemical means has been incomplete. The advent of more refined analytical procedures and tools are furthering efforts toward the identification of the constituents of orange oil in many laboratories.

Limonene oxide was found to be present in cold-pressed Florida Valencia orange oil by fractional distillation of the oil and comparison of the gas chromatographic retention times on columns packed with non-acid washed substrate and on capillary columns and infrared spectrum with those of known samples of limonene oxide.

It was observed that known samples of limonene oxide rearranged on gas chromatographic columns packed with acid washed support to products of unknown constitution. The infrared spectrum and gas chromatographic retention times of one of these products (I) were identical with those of an aldehyde found in the carbonyl fraction of orange oil and erroneously called rhodinal in a report made at the 1962 Citrus Processing Conference. A second of these isomerization products (II) was identified as dihydrocarvone by catalytic hydrogenation and comparison of the infrared spectrum of the reduced material to that of a known sample of tetrahydrocarvone and by comparison of the melting point of the oxime prepared from II with that of a known sample of dihydrocarvone oxime. Dihydrocarvone was also found in the carbonyl fraction of orange oil when care was taken to separate it from undecanal under which it largely occurred. The third isomerization product (III) was a ketone as indicated by infrared analysis and could not be related to any compound previously encountered in work here.

It was also observed that limonene oxide with zinc bromide in refluxing benzene yielded the same three products obtained in the gas chromatography of limonene oxide. Similarly, carvomenthene oxide reacted with zinc bromide in refluxing benzene to give an aldehyde (IV), carvomenthone (V),

and a ketone (VI). Reduction of I, II, and III to IV, V, and VI, respectively, verified that the two reactions proceeded in the same way.

The rearrangement and isomerization of epoxides to carbonyl compounds in the presence of alumina or Lewis acid catalysts is a well known reaction to both the bicyclic terpene oxide and the cyclohexane oxide series - the nature of the rearranged products being dependent upon the direction of the ring opening, the migratory aptitudes of the substituent groups, and the steric requirements of the molecule in question relative to a heterogenous catalyst. Royals and his co-workers and others have investigated the formation of dihydrocarvone and carvomenthone from limonene oxide and all have reported a number of six membered ring products. Because aldehydes I and IV and ketones III and VI were none of the products previously assigned to the rearrangement or isomerization of limonene oxide and carvomenthene oxide, this study was undertaken.

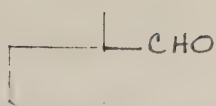
Aldehyde I was determined to be monomeric by carbon-hydrogen analysis. Quantitative hydrogenation gave aldehyde IV with the uptake of one mole of hydrogen per mole of aldehyde. The infrared spectrum indicated the presence of a terminal double bond by exhibiting strong absorption at 885 and 1625 cm^{-1} . The nuclear magnetic resonance spectrum showed

one singlet methyl at 70 cps., one allylic methyl at 103 cps., two unsplit vinyl protons at 380 cps., and one aldehydic proton unsplit at 564 cps. From these data it can be said that the structure contains no hydrogen alpha to the aldehydic group; one tertiary methyl group, and one terminal double bond. On the basis of these instrumental analyses, the structure 1-methyl-3-isopropenyl-cyclopentanal was assigned to I; and aldehyde IV must therefore be 1-methyl-3-isopropylcyclopentanal.

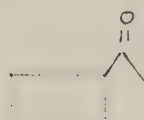
Aldehydes I and IV were oxidized to the corresponding acids, VII and VIII. Hydrogenation of VII also gave VIII which was subsequently identified as 1-methyl-3-isopropyl-cyclopentane carboxylic acid by synthesis from the known compound, 1-acetyl-3-isopropenylcyclopentene (IX). Compound IX was hydrogenated to 1-acetyl-3-isopropylcyclopentane. Comparison of the infrared spectrum obtained on the latter with that of ketone VI obtained from isomerization of carvomenthene oxide showed the two compounds were identical. Since ketone III yielded ketone VI on hydrogenation with the uptake of one mole of hydrogen per mole of ketone, and exhibited loss of terminal methyl group absorption in the infrared due to this reduction, III must be 1-acetyl-3-isopropenylcyclopropane. Ketone VI was methylated and subsequently oxidized to acid VIII. The gas chromatographic retention times and infrared

spectra of the methyl esters of the acids derived from the known compound IX and from aldehyde IV were identical, thus synthetically establishing aldehyde I as 1-methyl-3-isopropenylcyclopentanal and aldehyde IV as 1-methyl-3-isopropylcyclopentanal.

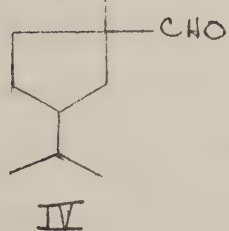
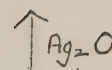
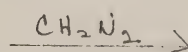
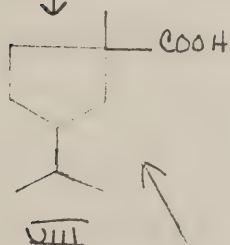
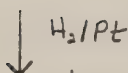
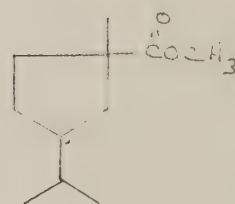
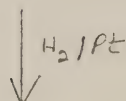
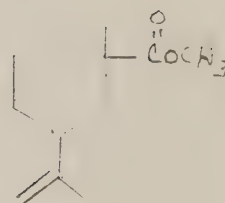
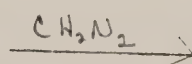
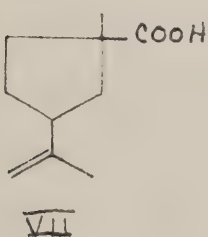
When limonene oxide was carried through the Girard's T procedure as used to separate carbonyls from other oxygenated terpenoids, it was found that limonene oxide was detectable in the carbonyl fraction. It is thus suggested that 1-methyl-3-isopropenylcyclopentanal and dihydrocarvone were artifacts derived from the isomerization and rearrangement of limonene oxide on the gas chromatographic column.



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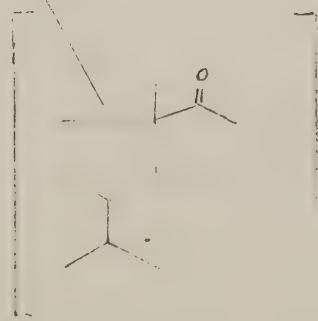
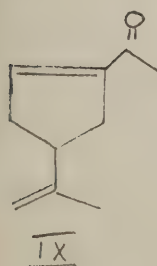
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Carvomenthene oxide



COUPLED GAS CHROMATOGRAPHY AND MASS SPECTROSCOPY AS AN
ADVANCED ANALYTICAL METHOD FOR CITRUS ESSENTIAL OIL ANALYSIS

by

G. L. K. Hunter and W. B. Brogden, Jr.
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Florida

Flavor - complex, evasive, discreet, dynamic, where miniscule modifications can create acceptance or rejection. What is it? How should it be studied? Is it possible?

The answers to these questions are encouraging. Flavor research is microchemical analytical research. It is research requiring the microseparation and identification of gross chemical mixtures, nothing more and nothing less. It is possible.

With the advent of gas chromatography, the most formidable half of this difficult problem has been overcome, i.e., the microseparation of gross mixtures. It is the second half, the identification of these micro species, which is the subject of this paper.

Visualization of the instrumental requirements for the identification of submicrogram quantities as rapidly as they are eluted from a gas chromatograph at first appears staggering. However, this too is now possible with the advent of the Bendix "Time-Of-Flight" mass spectrometer. This instrument is truly capable of unequivocal identification of submicrogram quantities of pure substances. The chemist has but

to interpret the data.

The Bendix "Time-Of-Flight" mass spectrometer, made available by the Florida Citrus Commission, operates simply by ionization of a gas by electron bombardment, the mean free path being extended by use of high vacuum (10^{-6} Torr), with a pulsed electron beam in the ionizing region of the ion source. The assorted batch of ions produced as a result of the electron impact is given an impulse of kinetic energy (acceleration) so that they are all directed down a field free tube toward a collector. All ions receive an equal energy impulse, therefore, their respective velocities vary according to their mass/charge ratio. The lighter ions have higher velocities. Since all ions leave the accelerating region simultaneously, those of equal mass will bunch together striking the collector. As each bunch strikes the collector cathode, secondary electron bunches are released. These are focused by electric and magnetic fields down the electron multiplier. The resultant amplified electron pulses are detected by an oscilloscope. The instrument is capable of pulsing ionizing electrons at the rate of 10,000 times a second resulting in 10,000 complete spectra every second.

Marriage of the gas chromatograph to the Time-Of-Flight Mass Spectrometer was inevitable. It was accomplished by splitting the gas chromatographic effluent stream through a

valve and directing a small fraction of the vapors into the ionizing region of the mass spectrometer. The remainder of the effluent may be directed to a gas chromatographic detector for simultaneous recording of the chromatogram. Since the gas chromatograph delivers a "peak" to the mass spectrometer for relatively long periods of time, it is possible to record the entire spectrum by use of a rapid scan recording system. The resulting spectrum can be analyzed and the "cracking pattern" compared with known patterns for positive identification. These patterns become standard when obtained under standard conditions. The last peak in the spectrum known as the "molecular ion" represents the unequivocal molecular weight of the substance.

This method has been successfully applied to the elucidation of the sesquiterpenes in both grapefruit and orange cold pressed oil. In order to simplify the analysis the oils were stripped of low boiling materials. The residue from this distillation was redistilled and the fraction containing the sesquiterpenes was collected. Examination of this fraction revealed the presence of carbonyls which were subsequently removed by column chromatography containing basic alumina in the usual manner.

Using the above procedure, known sesquiterpene hydrocarbons were obtained from various essential oils and their

cracking pattern recorded, providing reference spectra and knowledge of their mass spectral behavior. In the analysis of grapefruit sesquiterpene hydrocarbons, a two microliter sample was injected into a 500-foot capillary column operated isothermally at 155° C. with a helium pressure of 32 lbs/in². A gas chromatogram and mass spectra were recorded simultaneously as described above. As a result, positive identification was obtained for eight sesquiterpene hydrocarbons isolated from the grapefruit essential oil. Orange oil sesquiterpene hydrocarbon analysis was carried out in a similar manner. Three new sesquiterpenes were encountered and the structure of two have been elucidated. The remaining seven sesquiterpenes were identified.

The authors' initial experience into microanalytical chemistry using the new tools available to the chemist for such investigations has shown by the above work to possess great potential. Success will require patience, ingenuity and continued effort.

THE SESQUITERPENES OF LEMON OIL

by

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Fruit and Vegetable Chemistry Laboratory
Pasadena, California

Composition studies on cold-pressed citrus oils have greatly advanced in recent years through the use of gas chromatography on the volatile portion of the oil. Composition of the non-volatile portion of citrus oils also has been worked on extensively, particularly the crystalline solids. As a result of these studies approximately 90% of the weight of some citrus oils has been identified and assayed. Among the remaining portion still being studied is an interesting family of compounds, the sesquiterpenes. These compounds contain fifteen carbon atoms and are related biogenetically with the more familiar terpenes of citrus oils such as limonene and citral.

Although the sesquiterpene hydrocarbons and oxygenated hydrocarbons comprise only a few percent of the weight of cold-pressed citrus oils it is generally believed that they make a significant contribution to the flavor of these oils.

Initial studies on the chemistry of lemon oil sesquiterpenes have been directed toward the unsaturated hydrocarbons. Cold-pressed oil was folded under partial vacuum to about one-fourth its original volume in order to

remove most of the volatile terpene hydrocarbons. Passage of the folded oil through a column of chromatographic alumina in petroleum ether separated the unsaturated hydrocarbons from the oxygenated compounds. There was no evidence that the silicic acid or the basic, neutral or acid-washed alumina affected the terpene or sesquiterpene hydrocarbons. However, certain brands of silica gel caused considerable deterioration of the sesquiterpenes. Basic alumina should be avoided if the oxygenated fraction is desired subsequently without ester saponification.

After removal of the oxygenated compounds the hydrocarbon fraction was then distilled in a vacuum fractional distillation column to separate the sesquiterpenes, boiling range 70° - $90^{\circ}\text{C}/5$ mm Hg, from the remaining more volatile compounds and the less volatile waxes.

Examination of the sesquiterpene fraction by analytical gas chromatography revealed the presence of eight or more hydrocarbon compounds in the sesquiterpene region. The whole fraction was preparatively gas chromatographed on a $3/8'' \times 10'$ column packed with 60-80 mesh chromosorb P impregnated with 30% carbowax 20 M. Optimum temperature for good peak resolution and reasonable retention time fell between 170° and 180°C . The main fractions were repetitively rechromatographed for highest purity. Generally, a lower capacity analytical

column, 1/4" diameter, was necessary in the final step.

The three major sesquiterpenes in lemon oil were isolated in pure form and identified as β -bisabolene, γ -bergamotene and caryophyllene by comparison of their IR spectra and gas chromatographic retention times with those of known compounds.

Preparative gas chromatography was attempted with those sesquiterpenes present in lesser amounts, but considerable difficulties were encountered. Repeated high temperature gas chromatography on compounds potentially sensitive to such treatment necessarily calls for caution in the interpretation of results. Currently, new methods for separating the unsaturated hydrocarbons are being investigated.

TERPENE RESEARCH IN THE NAVAL STORES LABORATORY

by

G. S. Fisher

Southern Utilization Research and Development Division
Naval Stores Laboratory
Olustee, Florida

Like the Fruit and Vegetable Products Laboratory, the Naval Stores Laboratory at Olustee, Florida, is part of the Southern Utilization Research and Development Division of the Agricultural Research Service. This laboratory conducts a broad well balanced research program aimed at improving the utilization of pine gum and its components, i.e. of gum naval stores. This research is divided into three investigations: Pine Gum Investigations, headed by Mr. R. V. Lawrence who is also Chief of the Laboratory; Rosin Investigations, headed by Dr. G. W. Hedrick; and Turpentine Investigations, which I head. Since much of our research on the terpenes from gum turpentine is either directly or indirectly applicable to limonene, it seems appropriate to review it at this conference.

The two predominant terpenes in commercial turpentine are α - and β -pinene, but small amounts of limonene and other terpenes are also present. Similarly, citrus peel oils contain a preponderance of d-limonene but also contain small amounts of the pinenes and related terpenes. Methods of analysis developed for either turpentine or citrus peel oil are generally applicable to both products and the same pure

reference compounds are frequently needed by both groups. The Fruit and Vegetable Products Laboratory and the Naval Stores Laboratory regularly exchange reference samples and data with obvious benefits to the research programs of both Laboratories.

Through the years research in the Naval Stores Laboratory on the chemical transformations of the pinenes has almost routinely been accompanied by parallel studies on limonene. As many of you know, limonene can be made from the pinenes. Thermal isomerization yields dl-limonene but carefully controlled acid isomerization yields optically active limonene. New multimillion pound per year uses for limonene would certainly create increased markets for both citrus limonene and turpentine.

The remainder of this review will summarize some older examples of our research on limonene and related work on the pinenes rather briefly and describe a recent example in greater detail. During World War II, isoprene was made commercially from limonene. This process was based on research carried out by the Naval Stores Laboratory. In this investigation it was found that when limonene vapors were passed over a glowing wire grid, good yields of isoprene were obtained. The pinenes and other readily available terpenes gave very poor yields. However, less vigorous thermal isomerization of the pinenes give good yields of acyclic

terpenes. For a number of years, myrcene has been produced commercially from β -pinene by a pyrolysis process based on Naval Stores Laboratory patents. Similarly, allo-ocimene is produced commercially from β -pinene. The market for allo-ocimene is reported to be small but that for myrcene is over one million pounds per year.

In a general study, aimed at making light colored, high melting resins from turpentine, Dr. Goldblatt and his coworkers investigated the acid catalyzed polymerization of limonene and found that good resins could be made. It is our understanding that some resins of this type have been made commercially. They are similar but not identical with the more widely used β -pinene resins.

Much of our research on terpenes for the past several years has been devoted to some form of oxidation. Several years ago the Office of Rubber Reserve requested that we try to develop terpene hydroperoxides which could be used as catalysts in the synthetic rubber program. It was found that hydroperoxides could be made by simple autoxidation of the pinenes and of limonene and that they were good, but not outstanding catalysts. These hydroperoxides were mixtures and were not very stable. Further research revealed that hydrogenation of the terpenes before oxidation made the terpenes more resistant to oxidation but greatly enhanced their

activity as catalysts and their stability in storage. By this process, turpentine yields pinane hydroperoxide while limonene yields p-menthane hydroperoxide. At present, over two million pounds of p-menthane hydroperoxide is used annually in the production of synthetic rubber for passenger tires. Since p-menthane is available from wood naval stores by-products, we do not know how much limonene is being used for this purpose.

Because of interest on the part of the Defense Department in turpentine as a domestic replacement for imported raw materials for manufacture of synthetic lubricants, research on production of dicarboxylic acid from turpentine was initiated. This research resulted in the development of an improved process for production of the C_{10} methyl keto acid, pinonic acid, and the C_9 dicarboxylic acid, pinic acid, from α -pinene. Esters of the latter acid were satisfactory lubricants with good low and high temperature properties. The pinonic acid is made by ozonization of α -pinene followed by oxidative decomposition of the ozonide. Treatment with hypochlorites converts it to pinic acid. Many other derivatives of pinonic acid have also been made by the Naval Stores Laboratory. These include a C_{10} dicarboxylic acid, homopinonic acid, an amino acid which is useful as a modifier for Nylon-type polymers, a hydroxy acid whose vinyl esters can be copolymerized with vinyl chloride, and a series of

polymerizable esters of the other acids already mentioned. Most of these same reactions could be applied to limonene or to carvomenthene which can be made by controlled hydrogenation of limonene. In the case of limonene a unique diketo acid and a tricarboxylic acid would be expected.

As mentioned earlier in this paper, simple autoxidation of the terpenes gives complex mixtures. In seeking techniques which would give better yields of hydroperoxides and less complex mixtures, we were attracted to photosensitized oxidation. German workers had reported that α -pinene and β -pinene each yielded a single hydroperoxide if they were oxidized in dilute solution in the presence of strong visible light and small amounts of methylene blue or other sensitizers. We verified this and found that if natural chlorophyll or other oil soluble sensitizers were used, dilute solutions were not required. Use of undiluted terpenes greatly reduces the size of the reactors required to produce a given amount of hydroperoxide. Reduction of the hydroperoxides gives good yields of terpene alcohols which were formerly hard to prepare.

Recently we have investigated the photosensitized oxidation of carvomenthene and limonene. Typically, about 150 g. of terpene containing 0.5 g. of crude chlorophyll was oxidized at about room temperature in a water-cooled reactor which was internally illuminated by a water-cooled, 300-watt

incandescent light. About one-half the carvomenthene or limonene was oxidized in three hours, chiefly to the hydroperoxide. The hydroperoxides could be concentrated by removal of unreacted terpene under vacuum but were usually reduced to the corresponding alcohols with ethanolic sodium sulfite. In the case of carvomenthene the major alcohols obtained were trans-2-p-menthen-1-ol (29%), 1(7)-p-menthen-cis-2-ol (25%), 1(7)-p-menthen-trans-2-ol (17%) and trans-carvotanacetol (15%). Smaller amounts of cis-2-p-menthen-1-ol (9%), cis piperitol (2%), and carvomenthene epoxide (3%) were also isolated.

Limonene yields a similar mixture of alcohols, all of which contain an 8(9) double bond in addition to the double bond present in the corresponding alcohol from carvomenthene. The various alcohols obtained are precursors of carvone or of menthol and in general have pleasant odors themselves. Two additional new alcohols have been made by alkali isomerization of the 2,8(9)-p-menthadien-1-ols obtained from limonene. These have been identified as 2,4(8)-p-menthadien-1-ol and 3,8(9)-p-menthadien-1-ol.

To summarize, the Naval Stores Laboratory conducts a balanced program of fundamental and applied research on terpenes. While this program is primarily directed toward finding new outlets for α - and β -pinene, much of the information obtained can be applied to developing new products from

citrus limonene. When appropriate, new reactions and techniques are applied to limonene as well as to the pinenes. In addition to research by its staff, the Laboratory is conducting research on the application of the oxo reaction, the Prins reaction, and the hydroboration reaction to terpenes, including limonene, by contracts with leading universities.

Pertinent Publications

Vapor Phase Chemical Isomerization of α - and β -Pinene.

L. A. Goldblatt and S. Palkin, J. Am. Chem. Soc., 63, 3517 (1941).

The Continuous Thermal Isomerization of α -Pinene in the Liquid Phase. T. R. Savich and L. A. Goldblatt, *ibid*, 67, 2027 (1945).

Production of Isoprene from Turpentine-Derivatives.

B. L. Davis, L. A. Goldblatt and S. Palkin, Ind. Eng. Chem., 38, 53 (1946).

Peroxides from Turpentine as Catalysts for 5°C. GR-S Polymerization. G. S. Fisher, L. A. Goldblatt, I. Kniel, and A. D. Snyder, *ibid*, 43, 571 (1951).

Peroxides from Turpentine II. Pinane Hydroperoxide.

G. S. Fisher, J. S. Stinson and L. A. Goldblatt, J. Am. Chem. Soc., 75, 3675 (1953).

Correlation of Ultraviolet and Infrared Spectra of Terpene Hydrocarbons. R. T. O'Connor and L. A. Goldblatt, Anal. Chem., 26, (1954).

Terpene-derived Plasticizers. Preparation of Pinic Acid and Its Esters. V. M. Loeblich, F. C. Magne and R. R. Mod, Ind. Eng. Chem. 47, 855 (1955).

Peroxides from Turpentine. Production of Technical Grade Pinane Hydroperoxide. G. S. Fisher, J. S. Stinson, R. N. Moore and L. A. Goldblatt, ibid, 47, 1368 (1955).

Pinonic acid. Preparation by Ozonolysis of α -Pinene. G. S. Fisher and J. S. Stinson, ibid, 47, 1569 (1955).

Autoxidation of α -Pinene. R. N. Moore, C. Golumbic and G. S. Fisher, J. Am. Chem. Soc., 78, 1173 (1956).

p-Menthane Hydroperoxide. J. S. Stinson, G. S. Fisher and J. E. Hawkins, J. Org. Chem., 24, 1084 (1959).

Quantitative Determination of α -Pinene. R. L. Kenney, T. C. Singleton and G. S. Fisher, Anal. Chem. 31, 1676 (1959).

Pinonic Acid - A Promising Chemical Raw Material. G. W. Hedrick and R. V. Lawrence, Ind. Eng. Chem., 52, 853 (1960).

Reactions on an Alkaline Carbowax-20M Column. R. L. Kenney and G. S. Fisher, J. Gas Chromat., 1 (8), 19 (1963).

Photosensitized Oxidation of Carvomenthene. R. L. Kenney and G. S. Fisher, J. Org. Chem. In Press.

NEUTRAL CONSTITUENTS OF ORANGE PEEL JUICE EXTRACT

by

Lyle J. Swift

Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Florida

A study of the bitter flavors in orange peel is being made because of possible relationships to the flavor of citrus juices and other products. It has been established that peel juice can be detected at the 3 - 5% level when added to orange juice and that the effect is not favorable, but usually is described by panel members as bitter.

It has been previously shown in our laboratory that linalool and α -terpineol are the principal volatile constituents of peel juice that affect the flavor and a quantitative method was developed for their estimation. Since then attention has been shifted to the nonvolatile substances. It has been found that the bitter substances of peel juice can be extracted with benzene, but the extract so obtained is a very complex mixture. To simplify the problem, the extract was separated into phenolic, neutral, and lactone fractions. Because it is usually the largest and quite bitter, the neutral fraction, specifically, is the one that is considered here. The method of obtaining it is simple. The benzene extract is itself extracted with aqueous alkali to remove phenolic substances. The remaining benzene solvent is then

evaporated and the residue treated with aqueous ethanol and strong alkali and allowed to stand to change any lactone substances to their acid salts. After dilution the neutral substances are extracted with organic solvents.

The neutral fraction obtained as outlined above was chromatographed over a Celite column prepared according to the recommendations of Corbin, Swarz, and Keeney for their work on dinitrophenylhydrazones separations. This involves slurring the pre-dried Celite in isooctane and adding water and acetonitrile to form an immobile phase. After packing the column under air pressure, it was washed with isooctane previously equilibrated with acetonitrile. The sample was then added and development with the equilibrated isooctane carried out. Successive liters of eluate were evaporated in tared flasks and the eluates weighed. By plotting residue weights against liters collected, it was possible to establish peaks and then to bulk the residues making up single peaks into fractions. These were examined by ultraviolet spectrophotometry and identified where possible by comparison of the spectra with those of known compounds. In one case it was necessary to re-chromatograph one large fraction on a Magnesol column using a benzene-ethyl acetate mixture for development. Certain small fractions gave only generalized absorption in the UV and could not be crystallized and so were not

identified, but it was possible to account for nearly 80% of the neutral fraction. The results are given in the following table:

Tangeretin	4.9%
3,5,6,7,8,3',4' heptamethoxyflavone	6.1
Nobiletin	35.5
Sinensetin (5,6,7,3',4' pentamethoxyflavone)	24.2
Unidentified compound	8.6
	<hr/> 79.3%

The unidentified substance shown in the table above appears to be a single substance and some work has been done on its characterization, but it would be premature to discuss it in the present stage of investigation.

A search is being made for a chromatographic system, preferably thin-layer, that will separate the constituents of this fraction and perhaps permit their quantitative estimation. Some progress along this line has been made.

FOAM-MAT DRYING OF CITRUS AT ALBANY

by

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A 12-minute color movie presents the latest developments in the preparation of foam-mat dried orange solids. The developments include continuous foaming equipment modified by the addition of a wiped film cooler, minor modifications to the continuous dryer, and a hot rolling technique for densifying the orange powder.

Adding the wiped-film cooler to the foaming equipment has made it possible to produce very stable orange foams that resist breakdown and permit direct drying to 1 to 1.1% moisture without a scorched flavor. At this moisture, satisfactory material can be directly packaged without secondary drying or without an in-package desiccant.

The rolling techniques developed initially for foam-mat dried tomato were adapted for orange by applying 0.05 to 0.10% of monoglyceride release agent to the hot drum rolls. This rolled product after a light grinding has a bulk density of 0.8 to 0.9 grams/ml.

DEBITTERING GRAPEFRUIT JUICE BY MEANS
OF SPECIFIC ADSORPTION ON RESINS

by

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Polyamid resins such as Nylon or Perlon, and polyvinyl pyrrolidone polymers such as Polyclar AT, have a high affinity for tannins, leucoanthocyanidins and other flavonoid compounds. Use of such resins for debittering grapefruit juice has been demonstrated to be quick and efficient and not to materially change the flavor or composition of the juice other than to remove naringin and related flavonoids. Resin can be easily regenerated for reuse. Data on resin adsorption of naringin is presented.

FOAM-MAT DRIED ORANGE JUICE -- FURTHER STUDIES
OF DRYING CONDITIONS AND STORAGE STABILITY

by

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Progress has been made on the drying of frozen orange juice concentrate by the foam-mat process. Studies have been carried out to determine the effects of various physical factors on the drying capability of the concentrate. Concomitantly, investigations have been carried out on alterations in processing techniques which might result in improvement of storage stability of orange powders. Various types of analytical procedures have been examined to obtain more information about the nature of changes which occur upon storage of orange powders and subsequent development of "off-flavors."

In the studies concerning the factors affecting the physical nature of the concentrate as related to its drying ability, the effect of peel oil content was investigated. Orange powders with varying peel oil concentrations were test dried on the foam-mat dryer and the amount of moisture in the final powder was determined. It was found that under a given set of conditions a decrease in peel oil content resulted in more extensively dried powders.

In an analogous experimental series, the effect of pulp content on the drying ability was studied. Lower pulp content

was found to be advantageous to removal of moisture. To an orange concentrate sufficient centrifuge pulp was added to adjust the °Brix to several different levels. These were diluted to 50° Brix, foams were prepared, and they were dried on the foam-mat belt dryer. The final powders were analyzed for moisture and compared. Increased pulp content was found to decrease the degree of dryness achieved. These data may not be strictly typical as the concentrate used in this series was prepared from fruit which had been freeze damaged, but the trend shown is probably representative.

In another study of the effect of physical and chemical properties of the concentrate on its drying characteristics, the influence of Brix/acid ratio was determined. To two samples of an orange concentrate anhydrous citric acid was added to adjust the ratio to different levels. These samples and the original concentrate were dried and the amount of moisture in the final powder was determined. Higher acidity appeared to improve extent of drying, but differences were not felt to be great enough to be conclusive. There was no apparent heat damage and there were definite differences in degree of taste preference for the three samples.

Variations have been observed in the drying behavior of different concentrate samples which appear to be similar in most respects. This is shown by comparison of experiments

carried out on a concentrate obtained from fruit representing the 1961 season and a very similar one representing the 1962 season. A sample of orange concentrate obtained during the Valencia season in May of 1961 was dried and compared to one from a concentrate obtained in September of 1962, representing the Valencia season of '62. When dried under similar conditions, two samples of the concentrate from the 1962 season produced powders of lesser moisture content than that produced from the 1961 concentrate. There were similar differences noted in the rate of desiccation of these powders, in preparation for storage studies. The factors within these concentrates which are responsible for such differences are uncertain. These data serve to indicate, to some extent, the influence of seasonal variations on drying characteristics.

Further investigations were carried out in an attempt to improve the storage stability of orange powders. These included experiments in which the effects of production of foam, drying, and packaging in inert gas or packaging in vacuum were studied. Evaluation was based on detectable difference between controls and experimental samples. It appears that foam preparation in inert gas and packaging either in inert gas or in vacuum has little effect on extension of storage life of orange powders under the conditions studied.

As a further study in this respect, the effect of SO_2 was investigated, as well. Presence of SO_2 made very little difference in drying rate. Very little difference was found in the rate of desiccation at 70°F. over CaO . The storage times undergone before detectable differences were obtained between the control and experimental samples were only increased slightly in the samples treated with SO_2 . Thus, the improvement of storage stability by addition of SO_2 was not sufficient for that which would be required for a satisfactory product.

An investigation of methods for treatment of the powders in order to further reduce the moisture content to a desired level in a short time was undertaken. A system of secondary drying of orange powders was developed. This consisted of a rotating vacuum drum to contain the powder to be dried, with a central chamber for the desiccant. Using this apparatus several different ratios of orange powder to desiccant, desiccant types, temperatures of desiccation, reduced pressures and times of secondary drying were studied.

Studies have been initiated to determine whether analytical techniques could be applied to determine the nature of chemical differences occurring between control samples and those which have developed a processed flavor or storage "off-flavor." Variations in diacetyl number were checked in

samples during drying. The original diacetyl value in the concentrate was found to increase in different dried powders. The higher increases were in the samples where peel oil or SO_2 was added.

A gas chromatographic method has been developed which is based on extraction of powders with a mixture of solvents in a continuous extractor. The concentrated extracts from powders stored at 0°F . are analyzed by GC and compared to those obtained from powders which have been stored at 85°F . and which have developed definite characteristic "off-flavors." Differences have been found in three peaks, two of which are in relatively early, low temperature areas and one in the higher temperature region. In all three cases there is considerable reduction in size of peak in the "off-flavored" samples as compared to the control. More work is being carried out to determine how reproducible and representative these findings are, and to try to identify the nature of these constituents. There is the possibility that these may lead to suggestions for drying treatments or methods for evaluation of storage stability.

It may be concluded that low peel oil, low pulp content, and high acidity improve the extent to which moisture can be removed. The use of inert gas or SO_2 in processing and the use of inert gas or reduced pressure in packaging do not

appear to be of significant benefit in improvement of storage stability of orange powders. Measure of diacetyl content and application of gas chromatographic methods appear to hold some promise as tools for further study of the nature of changes occurring upon drying and storage and as possible methods for evaluation of quality or storage stability by objective means.

FOAM-MAT DRIED GRAPEFRUIT JUICE -- STUDIES OF FOAM
PREPARATION AND TIME AND TEMPERATURE OF DRYING

by

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The belt type foam-mat dryer was used for experimental drying of grapefruit concentrates. Using data from past experimentation with orange concentrates as a basis, methods for foaming of grapefruit concentrates were developed. The foams thus prepared were dried on the foam-mat dryer under various conditions of drying times and temperatures. The resulting powders were evaluated by analyses for moisture content, acidity, ascorbic acid content, and color. The samples were also evaluated organoleptically. Results indicated that grapefruit concentrate may not be quite as heat sensitive as orange concentrate, but nevertheless, is still susceptible to heat damage and precautions must be taken when it is dried.

Samples were also dried from two different concentrates under similar conditions and it was found that, as had been experienced previously with orange, there was considerable variation in drying capability of different concentrates. As a great number of these experiments were carried out on concentrate from fruit that had been freeze-damaged, the results may not be strictly typical. As evidence of this, an abnormally long desiccation period was found to be required

before the desired moisture level could be reached when samples were dried at 70° F. over CaO in preparation for storage studies.

Study of the drying characteristics of another more typical concentrate which had not been freeze-damaged indicated that moisture removal during foam-mat drying was at a much higher rate in this case. This sample will be studied to determine whether the desiccation rate is also more normal.

Using a "traveling" thermocouple imbedded into the foam layer, samples were dried under conditions of air temperatures such that the foam temperature was held nearly constant during a drying run. Grapefruit concentrate samples were dried at different foam temperatures. At each temperature several drying runs were made using different belt speeds such that a range of drying times was covered.

Some deviations from these drying times were necessary, especially in experiments carried out at higher temperatures where the very longest drying times could not be used due to heat damage. Organoleptic evaluation indicated that slight burnt flavor was present in the samples dried at the higher temperatures and longer times studied. Analyses for acidity as citric acid indicated an increase in total acidity in these same samples, the higher increase being in the sample dried for the longest time. Ascorbic acid content was reduced and

the color as measured by optical density was found to increase (darken) somewhat in the same samples in which acidity increased. All analyses of samples dried at lower ranges of temperatures and shorter drying times were found to show acidity, ascorbic acid content, and color measurements within a normal range.

The rates of moisture removal in different sections of the dryer were studied and compared between samples dried at similar belt speeds but at different temperatures. It was found that a slight increase in moisture removal rate was apparent as drying temperatures were increased. By far the greatest portion of moisture was removed in the early sections of the dryer (Sections A1 and A2) in every case.

In another study, the foam density was varied to determine whether a more complete moisture removal could be accomplished when a less dense foam was used. Similarly, the rate of loading of the foam onto the drying belt was varied to determine the relative effect of reduced loading on the drying ability of the foam. It was found that loading rate is probably not the limiting factor for degree of moisture removal in the ranges studied. Foam structure on the other hand appears to be a critical factor. More experimentation is being planned at present to clarify the influence of this factor on drying rates and amount of moisture removed.

There has been considerable interest shown in the market testing of these grapefruit powders. A consumer acceptance test is being planned to be carried out this winter in Western Germany and the United Kingdom in cooperation with the Florida Citrus Commission and the Market Testing Service of the U. S. Department of Agriculture. This study will be primarily directed toward determining the general consumer demand and acceptance of such a product.

UNITED STATES DEPARTMENT OF AGRICULTURE
AGRICULTURAL RESEARCH SERVICE

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